III.A.24 Innovative Seals for Solid Oxide Fuel Cells (SOFCs)

Objectives

- Select self-healing glasses for functionality as seals for SOFCs.
- Demonstrate functionality of the self-healing seals by leak tests.
- Measure stability of the self-healing glass in SOFC environments.
- Develop approaches to toughening self-healing glasses as seals for SOFCs.
- Survey commercial glasses suitable for making seals for SOFCs.

Approach

- Select glasses suitable for self-healing and expansion matching, measure thermophysical properties, prepare seals with SOFC components, and test seals over a range of temperatures including thermal cycles.
- Determine thermal stability of the glasses in SOFC environments, measure thermal properties after annealing, and fabricate seals for leak testing at cell operating conditions.
- Develop approaches for toughening sealing glasses through the reinforcing phase, select a reinforcing fiber, fabricate reinforced glasses, and incorporate toughened glasses into seals and seal tests.
- Perform literature search on glasses suitable for seals in SOFC.

Accomplishments

- Demonstrated ability of a self-healing glass in sealing SOFC components through leak tests over a range of temperatures between 25-800°C.
- Achieved ~300 thermal cycle between 25-800°C without leak of a self-healing glass and accumulated ~3,000 hours of hermetic cell performance at 800°C.
- These results provide great promise towards meeting SECA goals of seals for SOFCs.

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Introduction

A functioning SOFC requires seals that prevent electrode leakage and internal gas manifold leakage if internal gas manifolds are utilized. The seals must prevent the mixing of fuel and oxidant streams as well as prevent reactant escape to the surrounding environment. The seal material must be electrically isolating and be mechanically and chemically stable in contact with interfacing cell components in humid dual reducing and oxidizing conditions. Particular importance is the ability to seal between metallic and ceramic components with differing coefficients of thermal expansion (CTE), and do so while exposed to temperature transients over a range from room temperature up to SOFC operating temperature (≈800°C). This project is developing innovative sealing concepts for both short- and long-term functionality of SOFCs, addressing the aforementioned issues.

Approach

A novel concept of in situ crack healing by glasses is pursued in Phase I of the project. The fundamental idea underlying this concept is based on the fact that a glass with suitable low viscosity can heal cracks created by thermal expansion mismatch between materials that are being joined by a glass seal in a SOFC. The functionality of this innovative sealing approach based on in situ crack healing by a glass is demonstrated and quantified. Toughening and strengthening of the glass by fibers/particulates is pursued to minimize or eliminate bulk cracking of the seals. These concepts are pursued further in Phase I to address sealing capabilities and durability issues related to a functioning seal for a SOFC.

Results

Self-healing glasses were selected, fabricated, and used for making seals. A test fixture was constructed for leak testing and leak tests under appropriate SOFC test conditions were performed. The assembled system was successful in meeting the project goals of testing seals at both room and high temperatures. The results demonstrated self-healing behavior of seals with a significant capability for thermal cycles between 25 and 800°C. These results are very promising for meeting some of the goals of the SECA program for SOFCs. The details on these activities are given in the following.

In order to develop seals suitable for joining electrolyte (yttria-stabilized zirconia [YSZ]) to a metal using a glass that can show self-healing behavior requires selection of glasses with appropriate thermophysical properties and expansion match with YSZ and metals. A number of glasses were considered and synthesized. Samples of glass powders were used for x-ray diffraction studies to insure that the starting materials are indeed amorphous in crystal structure. The glass and YSZ powders were processed to fabricate samples for measurements of properties and testing. Expansion behaviors of all the samples, glasses, metals, and YSZ were measured between 25-1,000°C in a high-temperature dilatometer. The stability of glasses against crystallization was measured using an x-ray diffractometer after annealing samples in air and SOFC testing environments over extended time periods. Figure 1 shows the expansion behavior of a glass used in self-healing study and effect on annealing for 500 hours indicating insignificant change in the expansion behavior. The x-ray diffraction from annealed samples of glass indicated no crystallization, which is consistent with the expansion behavior.

The diffusion processes at high temperatures can heal cracks in ceramics and glasses. Crystalline ceramics require higher temperatures for healing than some of the glasses because of the thermally activated nature of the diffusion process responsible for healing. The self healing behavior was studied by heating the glass to desired temperatures between 25-1,000°C and observing the surface of the glass sample with cracks by a video camera (in a unique facility) for detecting the temperature-time history of the self-healing process to begin and end. These data were used for selecting the processing temperatures for making the seals and appropriate conditions required for demonstration of the self-healing behavior.

The leak test fixture developed was used for leak tests at room temperature and high temperatures. A seal was made using Crofer metal, Glass 4, and YSZ. The YSZ was sealed to Crofer by this glass and then the Crofer metal was welded to 304 SS housing. The inside of the SS 304 housing was connected to high-pressure side of the seal and the outside of the SS 304 housing was maintained at the atmospheric pressure. During the test the seal assembly was heated to the desired temperature inside a furnace and the seal was pressurized from inside for leak testing via monitoring the pressure as a function of time. The leak tests were performed at room temperature and at various temperatures during heating as well as during cooling. In addition, during the course of the leak testing the seal developed a small leak but the leak was repaired in situ in each case by keeping the seal at the test temperature. The seal has been tested further for its durability against thermal cycles and the results in Figure 2 show that the seal remained hermetic even after 271 thermal cycles and 2,900 hours of seal test at 800°C. The seal test was terminated after ~3,000 hours and 300 thermal cycles of testing and the post-test data showed that the glass remained amorphous even after such a long test indicating the potential of the glass for making self healing seals.

These results on thermal-cycle-ability of SOFC seals are quite promising for developing seals to meet the SECA goals for SOFCs.

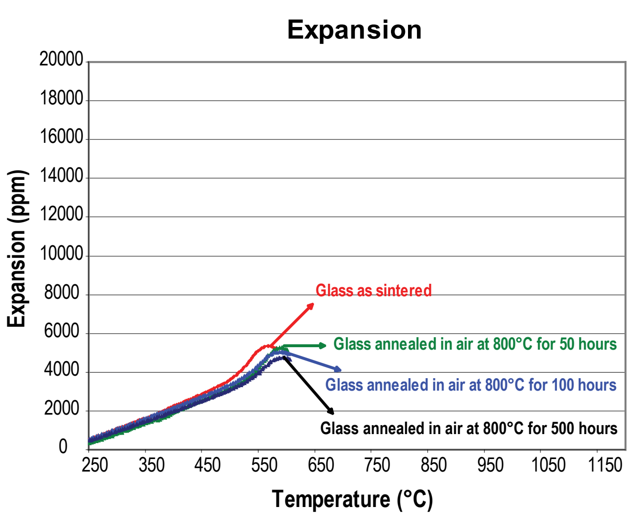

FIGURE 1. Effect of thermal annealing time at 800°C on the expansion behavior of a glass. Note an insignificant change in the expansion behavior.

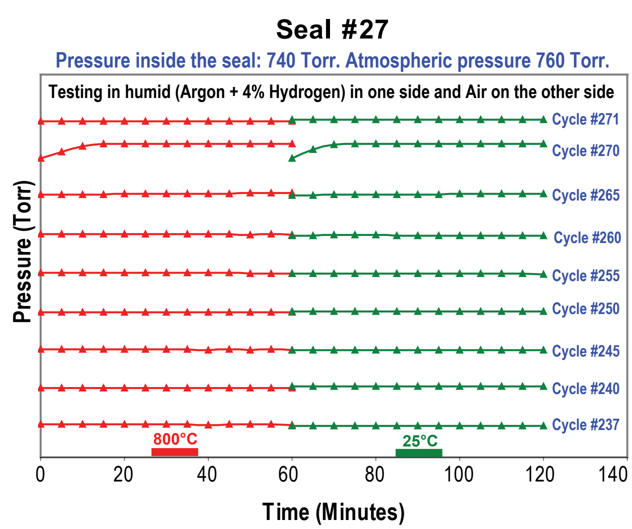

FIGURE 2. Pressure-time plots up to 271 thermal cycles of the leak tests at 800°C and 25°C of the seal made using Crofer-Glass-YSZ. This seal showed hermetic and self-healing behaviors even after 271 thermal cycles between 25-800°C. The data for each cycle shows pressure on the Y-axis vs time. A horizontal line for each cycle indicates hermetic response.

Conclusions and Future Directions

- Glasses were selected for demonstration of self-healing behavior and potential for making seals that display self-healing response. The thermal properties, densification behavior, and wetting behavior of glasses with YSZ electrolyte, Crofer, SS 430, and Nickel metals were determined for suitability of making seals.
- A new methodology based on video imaging of cracks was applied to characterize self-healing behavior of all the selected glasses and glass-ceramics as a function of temperature and time. Generally, glass-ceramics showed slower self-healing kinetics than the glassy state but the exact kinetics were dependent on the specific glass or glass-ceramics.
- Reinforced glasses were fabricated using alumina fibers. The effect of fiber addition to glass properties was characterized by dilatometer. Strengthening of the reinforced glass was demonstrated.
- Seals incorporating self-healing glasses were fabricated. Effect of up to ~300 thermal cycles between 25 and 800°C and ~3,000 hours at 800°C on hermeticity of the seals was demonstrated. Self-healing behaviors of the leaking seals were also demonstrated. These results are important for achieving the SECA goals of SOFC sealing systems.
- Plans are to pursue (in Phase II of the project) long-term stability of the self-healing glasses, reinforced glasses, and seals made thereof to further demonstrate long-term performance, stability, and applicability of the self-healing glass seals to SOFCs.

FY 2006 Publications/Presentations

1. Project Monthly Reports between October (2005)-March (2006).

2. Phase-I Program Report (December, 2005).

3. S. Parihar and R.N. Singh, "Self-Healing Glass Seals for Solid Oxide Fuel Cells", Proc. of Am. Ceram Soc. Annual Meeting (2005), in press.

4. R.N. Singh and S.S. Parihar, "Performance of Self-Healing Seals for Solid Oxide Fuel Cells," Ceram Eng. Sci. Proc. (2006), in press.